## REDUCING EMISSION OF METHYL BROMIDE FROM SOIL FUMIGATION: EFFECT OF A SHEET CONTAINING TITANIUM DIOXIDE

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Methyl Bromide (CH<sub>3</sub>Br) is a major fumigant in Japan to control soil-borne diseases in many crops. In last September, the international treaty was revised and signed that the use of CH<sub>3</sub>Br as a soil fumigant is to be phased out by 2005, and only some critical uses are permitted at present. But, no single chemicals or nonchemiclas alternative has yet emerged as a substitute for CH<sub>3</sub>Br in preplant soil fumigation. For now, 1,3-dichloropropene and chloropicrin are seen as the best alternatives to CH<sub>3</sub>Br for preplant fumigation in Japan, and sales of these alternative chemicals increases steadily year by year. However, the impact of these chemicals on the environment and human is not well understood, and these are considered risky and unacceptable as long-term replacements.

Such restrictions have led to an intensive search for improved technologies in CH<sub>3</sub>Br fumigation to reduce dosage and emission from fumigated plots into the atmosphere, while maintaining its effectiveness for disease and weed control. CH<sub>3</sub>Br emission reduction with field management practices, such as the use of gas-tight films, shallow injection (ca. 25 cm depth) in combination with irrigation, deep injection (ca. 60 cm depth), and application of ammonium thiosulfate or a soil bacterium, etc. have been tested. These methods can reduce the amount of CH<sub>3</sub>Br application and its emission during exposure period, and are appropriated injection methods.

In Japan, field sizes are generally small to apply machinery injection methods. Soil surface applications such as cold or hot gas methods are currently in use. Therefore, these techniques are not appropriate to Japanese horticulture. In previous studies we found that only the use of a gas-tight film (Orgalloy film, elf atochem) for the surface application considerably reduced emission loss to  $1.4\,\%$  of applied amount through the film and  $6.2\,\%$  from surrounding soil surface of treated area, that is,  $7.6\,\%$  in all emitted to the atmosphere during application (7 days), but large emission were observed just after removing the film,

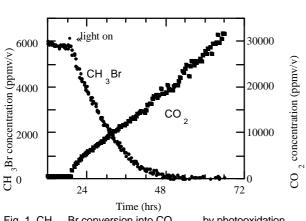
and it amounted to 33 % on the whole period. This result is not very different from that of conventional films such as

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polyethylene. The purpose of this study is to develop and evaluate the new multilayer sheet for surface application of CH<sub>3</sub>Br soil fumigant, which consisted of a impermeable layer, a titanium dioxide photocatalyst layer, and a support layer, from the upper to lower layer.

The impermeable layer to CH<sub>3</sub>Br was selected by measuring the transmittance of the ultraviolet light (400 nm or less). Titanium dioxide photocatalyst (ST-01, Ishihara Sangyo Kaisha, Ltd.) was spread ca. 3 g/m<sup>2</sup> on the non-woven high-density polyethylene fiber sheet (Tyvek, DuPont), then heat-sealed with a barrier film. This sheet was set up in the center of the separable chamber (10 cm in the effective irradiation diameter, the upper and lower chamber volume ca. 400 ml and ca. 280 ml, respectively) and then distilled water (1 ml) and CH<sub>3</sub>Br gas (2.5 ml) were introduced to the lower chamber. Irradiations were performed with a 500-W Xe arc lamp (Wacom) approximated to the AM1.5 G at room temperature. For measuring gas concentrations, two detectors were used: The Brüel & Kjær 1301 FT-IRphotoacoustic spectrometer (PAS) measured the concentration of CH<sub>3</sub>Br, carbon dioxide, water vapor. The gas chromatograph (GC) measured the concentration of CH<sub>3</sub>Br.

EVOH (60 μm: LDPE/ethylene-vinyl alcohol copolymer/LDPE) and fluorinated polymer films (50 µm) are excellent with respect to a barrier film and UV-transmittance, however, EVOH was selected because of facility in heat-sealing. CH<sub>3</sub>Br concentration at the beginning of examination was about 6000 ppm, 48 hours after the irradiation, it decreased to several ppm (Fig. 1). Some degradation products of CH<sub>3</sub>Br were identified as carbon



Br conversion into CO <sub>2</sub> by photooxidation

dioxide and hydrogen bromide. The decrease in CH<sub>3</sub>Br decomposition ability was observed during repeated use up to 5 times, because of detachment of titanium dioxide. It was possible to prevent these detachment by mixing with 10 % PTFE fine particles. Decrease in CH<sub>3</sub>Br concentration below the sheet was enhanced while covering

a field (7 or 9 days). Just before removing the sheet,  $CH_3Br$  concentration between the sheet and soil surface decreased to several ppm. This multilayer sheet can be repeatedly used for soil surface application methods and the problem in disposing the sheet is small. This technique is expected for commercial use.